Crossed Molecular Beams Studies of Phenyl Radical Reactions with Propene and trans-2-Butene

Daniel R. Albert, Michael A. Todt, and H. Floyd Davis*

INTRODUCTION

The reactions of phenyl radicals with propene have been studied at collision energies of 84 and 108 kJ/mol using the crossed molecular beams technique. The branching ratios between methyl radical elimination forming C₆H₅ and H-atom elimination forming C₆H₅₀ were found to be 10 ± 1:1 at 84 kJ/mol and 3 ± 1:1 at 108 kJ/mol. By using “soft” 9.9 eV vacuum ultraviolet photoionization for product detection, we were able to observe both product channels with negligible fragmentation of C₆H₅₂ to C₆H₅. Our finding that CH₃ elimination is dominant is consistent with conclusions from a recent study employing a pyrolysis molecular beam reactor using photoionization detection. However, our C₆H₅/C₆H₅₀ branching ratios are significantly larger than inferred from previous CMB experiments and RRKM calculations. For comparison, we have also studied the reactions of phenyl radicals with trans-2-butene at Eₜₐ₈ = 97 kJ/mol. In this case, the symmetry of trans-2-butene makes both alkene addition sites chemically equivalent. The intermediate formed in the reaction with trans-2-butene is similar to the 2-carbon addition intermediate in the reaction with propene. We observed only methyl elimination in the reaction with trans-2-butene, with no evidence for H-atom elimination, consistent with conclusions that C−C bond fission is the most favorable channel in these systems. Analogies between phenyl radical reactions with propene and trans-2-butene are used to provide insight into the mechanisms in the propene reaction.

ABSTRACT: The reactions of phenyl radicals with propene have been studied at collision energies of 84 and 108 kJ/mol using the crossed molecular beams technique. The branching ratios between methyl radical elimination forming C₆H₅ and H-atom elimination forming C₆H₅₀ were found to be 10 ± 1:1 at 84 kJ/mol and 3 ± 1:1 at 108 kJ/mol. By using “soft” 9.9 eV vacuum ultraviolet photoionization for product detection, we were able to observe both product channels with negligible fragmentation of C₆H₅₂ to C₆H₅. Our finding that CH₃ elimination is dominant is consistent with conclusions from a recent study employing a pyrolysis molecular beam reactor using photoionization detection. However, our C₆H₅/C₆H₅₀ branching ratios are significantly larger than inferred from previous CMB experiments and RRKM calculations. For comparison, we have also studied the reactions of phenyl radicals with trans-2-butene at Eₜₐ₈ = 97 kJ/mol. In this case, the symmetry of trans-2-butene makes both alkene addition sites chemically equivalent. The intermediate formed in the reaction with trans-2-butene is similar to the 2-carbon addition intermediate in the reaction with propene. We observed only methyl elimination in the reaction with trans-2-butene, with no evidence for H-atom elimination, consistent with conclusions that C−C bond fission is the most favorable channel in these systems. Analogies between phenyl radical reactions with propene and trans-2-butene are used to provide insight into the mechanisms in the propene reaction.

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1- and 2-carbon atoms, with the other ~15% coming from the methyl group. This result was consistent with expectations that H-atoms bound to the 1- and 2-carbon atoms in the adduct intermediate are more weakly bound than those in the methyl group.9

In a reinvestigation of the reaction of phenyl radicals with propene at a much lower collision energy (45 kJ/mol), methyl-elimination forming C8H8 was observed, along with the previously identified H-atom elimination pathways.16 The product branching ratio between the methyl and H-atom elimination was found to be ~2:1, in apparent agreement with RRKM calculations that accompanied the experimental work.16 The RRKM calculations predicted that methyl radical elimination forming styrene (C9H10) (calculated to be exergonic by 70 kJ/mol) should be dominant at low collision energies, with H-atom elimination forming C8H8 becoming dominant at collision energies above 100 kJ/mol. Possible isomers of C8H8 and their calculated energetics relative to the reactants are 2-phenylpropene (−31 kJ/mol), cis- and trans-1-phenylpropene (−24 and −32 kJ/mol) and 3-phenylpropene (−13 kJ/mol).16 In contrast to the earlier CMB study15 where 3-phenylpropene was found to be the minor H-atom elimination channel, this isomer was predicted by RRKM calculations to be the dominant C8H8 product.16 The preferential fission of the more strongly bound H-atoms from the methyl group (fission at the 3-carbon) was attributable to the potential energy barrier being about 1 kJ/mol smaller than for C−H fission at the 1- or 2-carbon atoms.16

In more recent work carried out at Berkeley’s Advanced Light Source, the reactions of phenyl radicals with propene were studied using a pyrolysis molecular beam reactor.17 Nitrosobenzene, which undergoes pyrolysis to form phenyl radicals and nitrogen monoxide, was coexpanded with propene carrier gas in a high temperature pyrolysis nozzle source where the phenyl radicals can subsequently react with propene. Products were probed using soft tunable vacuum ultraviolet (VUV) single photon ionization using a synchrotron. The authors were able to identify the methyl elimination channel forming C8H8, as well as H-atom elimination forming, C9H10. At the estimated temperature of the pyrolysis tube (1200−1500 K), formation of C8H8 was found to be dominant with a branching ratio of 6:1 for C8H8/C9H10. The contribution from C8H8 + CH3 relative to C9H10 + H inferred from the photoionization study is thus much larger than from the CMB study18 or from the RRKM calculations.16,18

Product photoionization efficiency curves can, under favorable conditions, be used to distinguish between chemical isomers having different ionization energies (I.E.).19 In the reaction of phenyl + propene, the C8H8 product produced in the pyrolysis molecular beam reactor was identified as styrene, the lowest energy C8H8 isomer.17 The photoionization efficiency curves for the C9H10 products were found to be consistent with primary formation of the 3-phenylpropene isomer, with a very small yield of the cis- and trans-1-phenylpropene (i.e., opposite to the previous CMB results16), with no evidence for production of the cyclic indane isomer.17

Here, we report studies of reactions of phenyl radicals with propene at collision energies of 84 and 108 kJ/mol using 9.9 eV single photon ionization of reaction products. To gain further insight into the C8H8 + C3H6 reaction, we also have performed CMB studies of the reaction of phenyl radical with trans-2-butene (C4H8).

### EXPERIMENTAL SECTION

The experiments were performed using the Cornell rotatable source, fixed detector crossed molecular beams apparatus, which has been described in detail previously.21 The phenyl radical beam (velocity = 2250 m/s; speed ratio = 13) was produced by bubbling H2 carrier gas (~1800 Torr) through room-temperature, liquid chlorobenzene (Sigma-Aldrich) (~10 Torr), expanding the gas mixture through the 1 mm orifice of a piezoelectrically actuated pulsed valve22,23 and photolyzing (6 mm × 2 mm spot size) chlorobenzene with the laser beam axis orthogonal to the molecular beam axis and aligned immediately in front of the pulsed valve orifice. The 193 nm photolysis of chlorobenzene produced primarily phenyl radicals and chlorine atoms.12,24,25 The 193 nm photons (~10 mJ per pulse) were generated with an ArF excimer laser (GAM EX10) that was attached to the rotating source flange in order to maintain constant alignment at all source angles. The phenyl radical beam passed through a 2 mm skimmer before entering the scattering chamber. Molecular beams of propene (Aldrich) and trans-2-butene (Aldrich) were generated by expanding a mixture of C8H8 or C9H10 in H2, or He carrier gas through a second 1 mm piezoelectric pulsed valve. Beam velocities, speed ratios, and collision energies for the C3H6 and C4H8 molecular beams are summarized in Table 1. The molecular beam passed through a 2 mm diameter skimmer before intersecting the phenyl radical beam at a 90° crossing angle.

<table>
<thead>
<tr>
<th>gas mixture</th>
<th>beam velocity (m/s)</th>
<th>speed ratio (v/Δv)</th>
<th>collision energy (kJ/mol)</th>
<th>CM angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25% C8H8 in H2</td>
<td>1050</td>
<td>12</td>
<td>84</td>
<td>14</td>
</tr>
<tr>
<td>9% C9H10 in H2</td>
<td>1700</td>
<td>10</td>
<td>108</td>
<td>22</td>
</tr>
<tr>
<td>25% C4H8 in He</td>
<td>960</td>
<td>12</td>
<td>97</td>
<td>17</td>
</tr>
</tbody>
</table>

The molecular beams were characterized in a separate series of experiments by chopping the beam with a slotted chopper wheel and measuring the on-axis time-of-flight (TOF) distributions using electron impact ionization detection.12 The phenyl radical beam and reactive scattering TOF distributions were measured using VUV photoionization detection. Scattered species traveled ~25 cm to a trially differentially pumped detector region (~10−10 Torr) where they were ionized using either the electron impact ionization detector or the VUV photoionization detector.26 The positive ions were then mass selected using a quadrupole mass filter (Extrel) and detected using a conversion dynode/electron multiplier in pulse counting mode.

The pulsed VUV light at 9.9 eV was generated by resonance enhanced four-wave mixing in Hg vapor through the two-photon resonance at 63 928 cm−1 using unfocused commercial lasers.26–28 The fourth harmonic (266 nm) of an injection seeded Nd:YAG laser (Continuum 9030) along with 380 nm light summed to the two photon resonance (63 928 cm−1), and a third photon (~630 nm) was tuned to phase match near the 9P resonance in Hg. The 380 nm radiation was generated by mixing the 580 nm output of a 532 nm pumped dye laser (Scanmate 2, Kiton Red dye) with the fundamental (1064 nm) of the seeded Nd:YAG laser. The 630 nm radiation was...
produced directly from a 532 nm pumped dye laser (Scanmate 2, DCM dye). All three lasers were aligned spatially and temporally through a 1 m long Hg heat pipe (~400 K). A slow flow of ~10 Torr of He buffer gas was maintained from the ends of the cell toward the center to keep the optics clean. The VUV was spatially dispersed from the ultraviolet and visible beams by off-axis transmission through a 50 cm focal length MgF2 lens (ISP Optics). The ultraviolet and visible beams were physically blocked from entering the detector by a ceramic beam dump mounted to a translation stage, while the VUV passed by the beam dump and entered the ionization region of the triply differentially pumped detector.

The TOF distributions were generated by stepping the VUV laser relative to the 193 nm photolysis laser. The product flux distribution was measured by rotating the source assembly relative to the detector and measuring TOF arrival distributions at each angle. Laboratory angular distributions were generated by integrating the TOF arrival distributions at each angle. The experimental data was fitted using the forward convolution technique described previously.29 A computer program took as inputs a center of mass translational energy distribution, \( P(E) \), a center of mass angular distribution, \( T(\Theta) \), and known instrument and beam parameters and outputted simulated TOF spectra and laboratory angular distributions. The two center of mass functions, \( P(E) \) and \( T(\Theta) \), were then iteratively adjusted until agreement was reached between the measured and simulated TOF spectra and laboratory angular distributions.

RESULTS AND DISCUSSION

\( \text{C}_9\text{H}_10 + \text{C}_6\text{H}_5 \) Experiments. The TOF distributions for \( \text{C}_9\text{H}_10 + \text{C}_6\text{H}_5 \) at \( E_{\text{coll}} = 84 \text{ kJ/mol} \), monitoring the formation of \( \text{C}_9\text{H}_{10} + \text{H} \) and \( \text{C}_6\text{H}_5 + \text{CH}_3 \), are shown in Figures 1 and 2, respectively. The H-atom elimination products were monitored at \( m/e = 118 \) (\( \text{C}_9\text{H}_{10}^+ \)) and methyl elimination products were monitored at \( m/e = 104 \) (\( \text{C}_6\text{H}_5^+ \)). The corresponding laboratory angular distributions are shown in Figure 3. The best fit CM functions for both channels are shown in Figure 4. The best fit \( T(\Theta) \) is forward-backward symmetric for both product channels, consistent with the participation of collision complexes with lifetimes greater than their picosecond rotational time scales. The isotropic angular distribution, i.e., a flat \( T(\Theta) \), is a consequence of angular momentum conservation and the geometric structure of the intermediate complex, as discussed in detail elsewhere.29 The best fit \( P(E) \) for the methyl elimination product channel peaks at ~35 kJ/mol, with a mean kinetic energy release of 48 kJ/mol. Thus, at this collision energy, 31% of the total available energy (154 kJ/mol) appears in product translational energy. For a 20 atom polyatomic system such as this, the appearance of a relatively large fraction of available energy in product translational energy suggests the existence of an exit barrier for the formation of \( \text{C}_9\text{H}_{10} + \text{CH}_3 \) consistent with theoretical predictions.9,16,18 The best fit \( P(E) \) for the H-atom elimination products is broad, with an average of 50 kJ/mol appearing in product translation. This corresponds to 43% of the available energy (115 kJ/mol), which again is a relatively large fraction for a polyatomic system of this complexity. We note that due to the kinematics of detecting a heavy species recoiling from an H-atom, the uncertainty in the \( P(E) \) is much larger than that for the methyl elimination channel.

The Newton diagrams for each product channel (Figure 5) illustrate the difference in the kinematics of the two product channels. The small Newton circle for H-atom elimination constrains the \( \text{C}_6\text{H}_{10} \) products to angles and velocities near that of the center of mass velocity vector. Consequently, the widths of the TOF and lab angular distributions are largely determined by the width of the center of mass velocity vector, especially in the case when the \( P(E) \) peaks near zero translational energy release. At a given angle, a larger fraction of the total H-atom elimination products are observed relative to those for methyl-elimination products (Figure 5). The product branching ratio at \( E_{\text{coll}} = 84 \text{ kJ/mol} \) was found to be 10 ± 1:1 for \( \text{C}_9\text{H}_{10}/\text{C}_6\text{H}_5 \).

The determination of product branching ratios must take into account the relative detection sensitivities for both products. In order to quantify the detection sensitivity for \( \text{C}_9\text{H}_{10} \) and \( \text{C}_6\text{H}_5 \) we have monitored nonreactive scattering of molecular beams of styrene (Aldrich, \( \text{C}_8\text{H}_8 \)) and alpha-methyl styrene (Aldrich, \( \text{C}_9\text{H}_{10} \)) using both a 100 eV electron impact ionization and 9.9 eV photoionization. By comparing the signal levels using both detection schemes, we found that the 9.9 eV photoionization cross-section for both species are equal to within our experimental uncertainty. This is not surprising as similar molecules belonging to a particular class (alkane, alkenes, monoaromatic species, etc.) often have comparable photoionization cross-sections at comparable energies above their ionization thresholds.30,31 We anticipate that the other possible \( \text{C}_9\text{H}_{10} \) isomers, all of which have ionization energies within 0.2 eV,17 have 9.9 eV photoionization cross-sections similar to alpha-methyl styrene.17,32

The dependence of internal energy on photoionization cross-section is relevant to the determination of product branching ratios.33–35 The total available product energy is the sum of the...
collision energy, internal energy of reactants, and reaction exoergicity. This energy is distributed among internal degrees of freedom (vibration, rotation, etc.) of the product species and relative translational energy. In the data fitting procedure, the translational energy distribution, \( P(E) \), is inferred; the total product internal energy distribution is found by subtracting the \( P(E) \) from the total energy available. In the \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \) reaction studied here, the total internal energy distribution is not much different for the \( \text{C}_8\text{H}_8 \) and \( \text{C}_9\text{H}_{10} \) reaction channels, ranging from 0 to 300 kJ/mol. The \( \text{C}_8\text{H}_8 \) product has a \( P(E) \) that peaks further from zero than the \( \text{C}_9\text{H}_{10} \) product and will thus have a slightly lower internal energy contribution. The largest effect of internal energy on photoionization cross-section is seen near the photoionization threshold.\(^{33−35} \) One obvious case of internal energy affecting the photoionization cross-section occurs with the ionization of product molecules below their 0 K ionization energy.\(^{33,34} \) In this case, vibrationally

Figure 2. TOF spectra monitoring \( \text{C}_8\text{H}_8^+ \) \((m/e = 104)\) from the \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \rightarrow \text{C}_8\text{H}_8 + \text{CH}_3 \) reaction, \( E_{\text{coll}} = 84 \text{ kJ/mol} \). Solid dots represent experimental data points; solid lines are calculated using the optimized CM distribution functions shown in Figure 4.

Figure 3. Laboratory angular distributions for the \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \) reaction, \( E_{\text{coll}} = 84 \text{ kJ/mol} \). Solid dots represent experimental data points with 1σ error bars. Solid lines are calculated using the optimized CM distribution functions shown in Figure 4. (a) \( \text{C}_9\text{H}_{10}^+ \) \((m/e = 118)\) from the \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \rightarrow \text{C}_9\text{H}_{10} + \text{H} \) reaction. (b) \( \text{C}_8\text{H}_8^+ \) \((m/e = 104)\) from the \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \rightarrow \text{C}_8\text{H}_8 + \text{CH}_3 \) reaction.

Figure 4. Optimized CM distributions for the \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \) reaction, \( E_{\text{coll}} = 84 \text{ kJ/mol} \). (a) \( P(E) \) for the \( \text{C}_9\text{H}_{10} \) products; (b) \( P(E) \) for the \( \text{C}_8\text{H}_8 \) products; and (c) \( T(\Theta) \) used for both \( \text{C}_9\text{H}_{10} \) and \( \text{C}_8\text{H}_8 \) products.

Figure 5. Newton diagram for the \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \) reaction, \( E_{\text{coll}} = 84 \text{ kJ/mol} \). Dotted circle corresponds to the maximum \( \text{C}_9\text{H}_{10} \) velocities from \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \rightarrow \text{C}_9\text{H}_{10} + \text{H} \). Solid circle corresponds to the maximum \( \text{C}_8\text{H}_8 \) velocities from \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \rightarrow \text{C}_8\text{H}_8 + \text{CH}_3 \).
excited neutrals now have sufficient energy to reach the ground state of the ion, where their vibrationally unexcited counterparts do not. Also, when just above threshold, Franck–Condon factors can significantly affect the ionization efficiency if the ion has different equilibrium bond lengths than the neutral. Recent studies probing this behavior have found that when molecules are ionized using single photon ionization that is well above the ionization threshold (>1 eV), the ionization efficiency is relatively independent of internal energy. In the detection of C₈H₈ and C₉H₁₀ at 9.9 eV, photoionization is carried out ~1.5 eV above the ionization threshold, and we do not expect the photoionization efficiency to be significantly altered by the internal energy of the products.

Both channels were also observed from the C₆H₅ + C₃H₆ reaction at E_{coll} = 108 kJ/mol. Time-of-flight arrival distributions for C₆H₁₀ + H and C₈H₈ + CH₃ are shown in Figures 6 and 7, respectively. The lab angular distributions for both product channels are shown in Figure 8. The best fit center-of-mass angular distributions are again isotropic for both channels. The P(E) for the C₆H₅ + CH₃ channel again peaks away from zero translational energy release (Figure 9). At this collision energy, 28% of the total available energy (178 kJ/mol) appears in product translational energy, which is similar to the value (31%) observed at the lower collision energy. Unfortunately, because of the kinematics of the H-atom channel, there is substantial uncertainty in the P(E), particularly in the region of low translational energy at the higher collision energy. We used the same P(E) for the H-atom channel at E_{coll} = 108 kJ/mol as was derived from the 84 kJ/mol data. The product branching ratio at E_{coll} = 108 kJ/mol is 3 ± 1:1 for C₆H₅/C₆H₁₀. Even at the increased collision energy of 108 kJ/mol, we thus measure a substantially larger contribution for the C₆H₃ channel than was predicted by RRKM calculations and measured in a previous crossed molecular beam scattering experiment by Kaiser et al. at E_{coll} = 45 kJ/mol where a 2:1 branching ratio was measured. While we have not studied the reaction at collision energies below 84 kJ/mol, from the observed trend observed in our study we would anticipate branching ratios greater than 10:1. One complication in detecting the C₈H₈ product channel in the previous study using 80 eV electron impact was background from fragmentation of C₆H₁₀ to the parent mass of C₆H₈. We are able to eliminate the fragmentation problem by using soft photoionization at 9.9 eV. Since the ionization energies of C₆H₈ and C₆H₁₀ are both near 8.5 eV, the use of photon energy close to the ionization threshold of the detected species minimizes dissociative ionization, allowing products to be detected exclusively at their parent mass.

In the C₆H₅ + C₃H₆ reaction, the phenyl radical can add to either the 1- or 2-carbon atom in propene, as illustrated in Figure 10a,b, respectively. On the basis of the calculations of Park et al. and Kaiser et al., the addition to the 1-carbon proceeds over a slightly smaller barrier than the addition to the 2-carbon (5 kJ/mol for the addition to the 1-carbon and ~10 kJ/mol for 2-carbon addition). In previous papers, considerable significance was attached to the relative barrier heights for addition, and mechanisms all focused on the 1-addition process as being dominant. However, in the crossed molecular beams experiments to date, the collision energies are far above both the 1- and 2-addition barriers. Furthermore, it is well-

![Figure 6](image.png)

**Figure 6.** TOF spectra monitoring C₆H₅⁺ (m/e = 118) in the C₆H₅ + C₃H₆ → C₆H₁₀ + H reaction, E_{coll} = 108 kJ/mol. Solid dots represent experimental data points; solid lines are calculated using the optimized CM distribution functions shown in Figure 9.

![Figure 7](image.png)

**Figure 7.** TOF spectra monitoring C₈H₈⁺ (m/e = 104) in the C₆H₅ + C₃H₆ → C₆H₁₀ + H reaction, E_{coll} = 108 kJ/mol. Solid dots represent experimental data points; solid lines are calculated using the optimized CM distribution functions shown in Figure 9.

![Figure 8](image.png)

**Figure 8.** Laboratory angular distributions for the C₆H₅ + C₃H₆ reaction, E_{coll} = 108 kJ/mol. Solid dots represent experimental data points; solid lines are calculated using the optimized CM distribution functions shown in Figure 9. (a) C₆H₅⁺ (m/e = 118) from the C₆H₅ + C₃H₆ → C₆H₁₀ + H reaction. (b) C₈H₈⁺ (m/e = 104) from the C₆H₅ + C₃H₆ → C₆H₁₀ + CH₃ reaction.
established that a low energy isomerization pathway allows rapid conversion between the 1-carbon vs 2-carbon addition intermediates. This was confirmed in a recent RRKM study, which found that the rate constant for isomerization is substantially faster than decomposition. Under these conditions, the relative importance of the addition to the 1-carbon or 2-carbon should not play a major role in determining the branching ratios between products. This conclusion is supported by comparisons of RRKM branching ratios assuming exclusive addition to the 1-carbon or 2-carbon atoms, which found that the branching ratios are nearly identical in both cases. At very high collision energies (e.g., 200 kJ/mol) the product branching ratio for CH₃ elimination to H-atom elimination changes from 1:3.5 for exclusive addition to the 1-carbon to 1:2 for exclusive addition to the 2-carbon. On the basis of these results, under our experimental conditions the initial phenyl radical addition site (1-carbon or 2-carbon) should have minimal influence on the final product branching ratios due to rapid isomerization. However, in discussing the reaction mechanisms, and in making comparisons with reactions involving trans-2-butene, it is important to remember that the 1-carbon and 2-carbon addition intermediates decay by different reaction pathways, with the 1-carbon intermediate decaying by R1 and R2, and the 2-carbon intermediate decaying by R3 and R4, as summarized in Figure 10.

As shown in Figure 10a, the most likely products from the 1-carbon addition intermediate involves formation of C₆H₅(CH₃)₂ isomers (1-phenylpropene (R1) or 3-phenylpropene (R2)) by H-atom loss. From the 2-carbon addition intermediate (Figure 10b), because of the much weaker C−C bond relative to C−H, the likely decomposition product is C₆H₅CH₂H (R4), with H-atom loss producing 2-phenylpropene (R3) also possible. While we find the C₆H₅(CH₃)₂/C₆H₅CH₂H branching ratio to be larger than in the previous crossed beams study and the accompanying RRKM calculations, we observed a decrease from 10:1 at $E_{\text{coll}} = 84$ kJ/mol to 3:1 at $E_{\text{coll}} = 108$ kJ/mol, consistent with the trend observed in the previous RRKM calculations.

C₆H₅ + C₄H₈ Experiments. In an effort to gain additional insight into the propene reaction, we have also studied the phenyl radical reaction with trans-2-butene (C₄H₈). For this reactant, the 2- and 3-carbon atoms are chemically equivalent, and addition at both sites produces a common reaction intermediate, as illustrated in Figure 10c. This intermediate resembles that of the 2-carbon addition intermediate in the C₆H₅ + C₃H₆ reaction, (Figure 10b), due to the presence of both an H and CH₃ at the carbon atom addition site. The C₉H₁₀ TOF arrival time distributions at $E_{\text{coll}} = 97$ kJ/mol for the reaction C₆H₅ + C₄H₈ → C₉H₁₀ + CH₃ are shown in Figure 11. The resulting laboratory angular and CM distributions are shown in Figures 12 and 13, respectively. The $P(E)$ peaks away from zero near 50 kJ/mol, implying that an exit barrier exists for the methyl elimination pathway. This is consistent with the behavior observed for the methyl-elimination channel in the C₆H₅ + C₃H₆ reaction. The $T(\Theta)$ is isotropic, suggesting the participation of collision complexes with lifetimes exceeding their rotational periods, as was observed in the propene reaction.
We carefully searched for the reaction \( \text{C}_6\text{H}_5 + \text{C}_4\text{H}_8 \rightarrow \text{C}_{10}\text{H}_{12} + \text{H} \) but found no evidence for its existence. Because of the kinematics of the reactions, our detection sensitivity for the H-atom elimination channel should be more than an order of magnitude larger than for methyl elimination. The photoionization cross-sections for phenyl products are similar, so no significant difference in detection sensitivity from differing photoionization cross-sections should exist. \(^{30,31}\) From these considerations, we conclude that the H-atom elimination channel from \( \text{C}_6\text{H}_5 + \text{C}_4\text{H}_8 \) cannot account for more than 3\% of the total reaction cross section. The dominance of C–C bond fission relative to C–H bond fission in these systems is a direct consequence of the much smaller C–C bond energy relative to C–H, as well as the smaller potential energy barrier for C–C bond fission relative to C–H fission. We now examine the reasons underlying the fact that C–H bond fission is observed in the propene reaction but not in the \textit{trans}-2-butene system.

**Propene Reaction Mechanism.** The absence of the H-atom elimination channel in the \textit{trans}-2-butene reaction is useful in understanding the propene reaction. The channels originating from the 2-carbon addition intermediate in the \( \text{C}_6\text{H}_5 + \text{C}_4\text{H}_8 \) reaction (Figure 10b) have analogues in the \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \) reaction (Figure 10c): R3 is analogous to R5 because both involve H-atom elimination from the carbon atom adjacent to the phenyl group. Similarly, R4 is analogous to R6 because both involve CH3 elimination from the carbon atom adjacent to the phenyl group. The \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \) reaction intermediate can also lose a hydrogen atom from the methyl group (R7 in Figure 10) in a manner analogous to the \( \text{C}_6\text{H}_5 + \text{C}_3\text{H}_6 \) reaction (R2 in Figure 10) forming 3-phenylpropene. Reaction R1 in the propene system, involving H-atom elimination from a CH2 moiety adjacent to the phenyl group, has no analogue in the butene system.

In the comparison of the butene and propene reactions, one must keep in mind that the cis steric repulsions in the alkene products differ slightly between the propene and butene systems, with the cis-methyl−methyl and methyl−phenyl repulsive interactions being slightly more important in the butene reactions. From these considerations, the H-atom elimination channels in the butene reactions are slightly less thermodynamically favorable (by a few kJ/mol) than are the analogous products in the propene system.

As noted above, the absence of H-atom products from the \textit{trans}-2-butene reaction shows that the H-atom elimination reactions R5 and R7 cannot compete with the methyl elimination channel R6. Because of the above-noted similarity between intermediates in Figure 10b,c, H-atom elimination from the 2-carbon addition intermediate (R3) is not likely to be competitive with CH3 elimination (R4). Despite the slightly different (at most a few kJ/mol) energetics between the propene and butene reactions due to the cis-steric interactions, the butene results provide strong evidence that H-atom elimination in the propene reaction primarily results from decomposition of the 1-addition intermediate, as illustrated in Figure 10a (R1 and R2).

Our finding that R7 is not competitive with R6 in the butene system is also of value in deriving insight into the propene...
reaction. The H-atom elimination pathway R7 for butene is analogous to R2 in the propene reaction, which is believed to be the sole source of 3-phenylpropene. In drawing conclusions from these analogies, it is important to remember that in the butene system, all products are formed from chemically indistinguishable reaction intermediates (Figure 10c) and are in direct competition with one another. In contrast, H-atom elimination in the propene system via R2 is only in direct competition with R1, and any competition between R2 and the other available channels (R3 and R4) requires isomerization between the 1- and 2-addition products. As noted above, the low barrier for isomerization and the RRKM calculations provide strong evidence that isomerization is much faster than product formation by bond fission under our experimental conditions.16 Under such limiting conditions, all four decomposition pathways (R1−R4) can be considered to be in mutual competition, in a manner analogous to the competition (R5−R7) in the butene reaction. From the analogies between R7 and R2, as well as between R5 and R3, described above, we are thus tempted to suggest that in the propene system, the H-atom channels, R2 and R3, are not likely to be competitive with CH3 elimination, R4. This would lead to the conclusion that in the propene system, the dominant source of H involves R1, which has no analogue in the trans-2-butene reaction, and that the dominant C9H10 isomers are cis- and trans-1-phenylpropene. This conclusion is consistent with the earliest crossed beam studies using deuterated propenes, which reported an 85:15 branching ratio for 1-phenylpropene/3-phenylpropene.15 However, more recent RRKM calculations have instead suggested the reverse behavior, with the 3-phenylpropene dominating the chemistry because of a slightly (∼1 kJ/mol) smaller barrier for its production via C=H bond fission.16,18

In the newer CMB study at Ecoll = 45 kJ/mol, the branching ratios for H or D atom elimination from the different propene carbon atom sites were not reported.16 However, in the recent photoionization efficiency studies using tunable synchrotron radiation, it was found that the experimental data could be simulated by assuming dominant formation of 3-phenylpropene (I.E. = 8.40 eV), in apparent support of the newer electronic structure and RRKM calculations.17 However, because of the similarity in the ionization energies for the different isomers,17 other possible isomer branching ratios would also be consistent with the experimental measurements, including dominant formation of trans-1-phenylpropene (I.E. = 8.38 eV).17

While our observations appear to support the earlier CMB study in which 1- and 2-phenylpropene were identified as the primary C9H10 isomers, with only minor formation of 3-phenylpropene,15 the use of soft 9.9 eV photoionization detection of products from crossed-beam studies employing D isotope labeled propene would provide more definitive conclusions. We hope to carry out such studies in the future.

According to the previous calculations, phenyl radicals can abstract hydrogen atoms from propene forming C6H6 (benzene) + C3H5, with several different isomeric forms of C6H6 radical possible.9,16,18 Abstraction of one of the three methyl H-atoms forming resonantly stabilized allyl radicals is most favorable energetically, with abstraction at the sp2-hybridized carbon atoms leading to formation of 1- and 2-propenyl radicals.9,18 To date, none of the CMB studies have addressed these channels. In principle, these channels can be most easily monitored by detecting C6H6 at its parent mass, m/e = 78. Unfortunately, because of the natural abundance of 13C, background signals due to elastic and inelastic scattering of C6H6 is present, with intensities ∼6% of that at m/e = 77, making it impossible to detect nascent benzene from the abstraction channel at m/e = 78. However, using deuterated propene, abstraction of a D-atom produces C6D6D, which can be detected with high sensitivity at m/e = 79. Furthermore, by comparing the signals at m/e = 79 from reactions of 3,3,3-trideuteropropene to that from 1,1,2-trideuteropropene, it should be possible to assess the relative importance of abstraction at the methyl vs sp2-hybridized carbon atoms in propene.

## CONCLUSIONS

In the reaction of phenyl radicals with propene, both H-atom and CH3 elimination products were observed at collision energies of 84 and 108 kJ/mol. At both collision energies, methyl radical elimination forming C6H6 was found to be dominant, with branching ratios for C6H5/C6H4 of 10 ± 1:1 and 3 ± 1:1 at 84 and 108 kJ/mol, respectively. The decrease in product branching ratio with increasing collision energy is consistent with RRKM predictions.16 However, we find the methyl radical elimination channel to be considerably larger than inferred from the previous CMB studies16 but comparable to those measured in a high-temperature pyrolysis reactor.17

Further insight into the reaction mechanism was gained by studying the reaction of phenyl radicals with trans-2-butene, where addition at each carbon atom leads to indistinguishable intermediates analogous to the 2-carbon addition intermediate in the propene reaction. In the reaction with trans-2-butene, elimination of CH3 forming C6H10 was observed with an upper limit of 3% for the H-atom elimination products. From analogies between the open reaction channels in the propene and trans-2-butene reactions, we suggest that in the reaction with propene that the minor H-atom elimination channel results from decomposition of the 1-carbon addition intermediate. While we tentatively suggest the reaction involves fission of the weakest C−H bond, producing cis- or trans-1-phenylpropene, definitive conclusions regarding the isomeric form of the C6H10 product and the mechanisms for the abstraction reactions forming benzene await deuterium isotope labeling studies.

## AUTHOR INFORMATION

**Corresponding Author**

*(H.F.D.) E-mail: hfd1@cornell.edu.*

**Notes**

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